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DECOMPOSITION OF GD ON CeO_2 /ALUMINA ADSORBENTS IN A GAS CHROMATOGRAPH ON-COLUMN INJECTOR TUBE REACTOR

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14. ABSTRACT The decomposition of GD on alumina supported CeO ₂ was determined at 25 °C in a quasi micro-reactor. One microliter of GD solution (50% by weight in carbon tetrachloride) was injected into a CeO ₂ /alumina (~ 40 mg) packed inlet tube of a Perkin Elmer Auto M Gas Chromatograph and maintained at 30 °C. A Nicolet 800 Bench Spectrometer with a mercury-cadmium-telluride detector (11,700 to 600 cm ⁻¹) was used to monitor the effluent. An injection was made approximately every hour until GD was detected. The adsorbent was then extracted with acetonitrile and the solution treated with BSTFA to esterify any hydrolysate; the mixture was assayed by GC/MS. The GD (521 µmol/g) was decomposed on CeO ₂ /alumina; the major products were pinacolyl methylphosphonic acid, methyl phosphonic acid, and dipinacolyl methylphosphonate.														
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PREFACE

The work described in this report was authorized under Project No. 206023-84BPO/CB2, Non-Medical CB Defense. The work was started in June 2003 and completed in September 2003. The data was recorded in laboratory notebook numbers 01-0133 and 98-0034.

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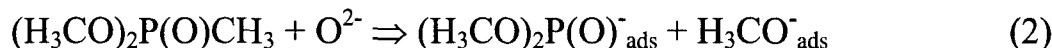
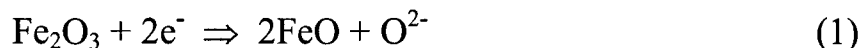
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DECOMPOSITION OF GD ON CeO₂/ALUMINA ADSORBENTS IN A GAS CHROMATOGRAPH ON-COLUMN INJECTOR TUBE REACTOR

1. INTRODUCTION

The dissociative adsorption of chemical agents on microcrystalline and nanocrystalline metal oxides yields the hydrolysate of the parent phosphorous compound as the major product.^a The rate of reaction of G and V type agents is a function of hydroxyl strength and diffusion rate of the adsorbate. Site defects might contribute to reactivity in nanocrystalline adsorbents; however, this hypothesis has not been verified at the U.S. Army Edgewood Chemical Biological Center (ECBC). The decomposition of GD and VX on Al₂O₃ (e. q. most recent version of the M295 kit) and nanosize MgO is extremely fast under certain conditions.^{b, 1}

Mitchell and co-workers at Clark Atlanta University have taken an alternative approach to reactive adsorbents. Iron oxide and mixtures of Fe₂O₃ and CeO₂ on aluminum oxide were reported to cleave the P-C and P-O bonds in dimethyl methyl phosphonate (DMMP) at room temperature.^{2, 3} Mitchell proposed that P-C bond cleavage was due to the participation of the lattice oxygen and that the mechanism proceeded by the Mars-van Krevelen route.⁴ The mechanism is due to a change in the oxidation state of the metal, which creates a low-energy pathway for nucleophile oxygen (O²⁻) to react with the adsorbate (DMMP).² An example of the Mars-van Krevelen mechanism for the decomposition of DMMP on Fe₂O₃/alumina is shown in schemes 1 and 2.²



The reaction occurs only when the weight of iron on alumina is between 7.5 and 8.5 %.⁵ In subsequent experiments, Mitchell reported that the addition of cerium oxide to Fe₂O₃/alumina increased the decomposition yield of DMMP, and that alumina-supported CeO₂/alumina was even more reactive. Analysis of the CeO₂ phase determined that the yield of reaction products was a result of amorphous and not crystalline CeO₂.³ The reaction rates at

^a Other products or by-products are the anionic leaving group and the adjacent O-ester group, e. q. the diisopropylaminoethylthiol group and possibly the ethoxy group from the decomposition of VX. The product in this case would be methylphosphonic acid (MPA). Under controlled laboratory conditions, HD reacts with metal oxides to yield divinyl sulfide, 2-chloroethyl vinyl sulfide, and thiodiglycol. The distribution of products is a function of the amount of water on the adsorbent, which is determined by the ambient humidity, exposure time of adsorbent to air before decontamination, and the temperature of adsorbent calcination. As the calcination temperature increases, the basicity of the surface hydroxyls increase and decomposition of HD by these groups occurs by an elimination mechanism and not substitution (hydrolysis).

^b The adsorbents were rubbed across either VX or GD (surface density and amount of sorbent) contaminated surfaces at room temperature and the reaction of agent on the sorbent was followed by ³¹P NMR. Typically, no agent was detected in the first spectrum approximately 15 minutes after the surface decontamination procedure.

room temperature of GD on $\text{Fe}_2\text{O}_3\text{-CeO}_2/\text{alumina}$ and A-200 were similar in tests at ECBC; the mechanism and products were not ascertained.⁶

In this paper, the yield and products from the decomposition of GD on $\text{CeO}_2/\text{alumina}$ are reported. Decomposition of gaseous GD in helium over $\text{CeO}_2/\text{alumina}$ was accomplished at 25 °C. The helium flow was monitored continuously by FTIR on the downstream side of the $\text{CeO}_2/\text{alumina}$ bed until GD was detected. The adsorbent was then extracted with acetonitrile and assayed by GC/MS.

2. EXPERIMENTAL PROCEDURE

A small amount of glass wool was first placed within the inner area of the Perkin Elmer glass inlet tube at the constriction (illustration 1) and packed slightly to inhibit the progression of the adsorbent into the column of the gas chromatograph. A small amount of the adsorbent (approximately 40 mg) was inserted into the tube on top of the glass wool plug. The adsorbent tube was tapped on the side to gently pack the adsorbent. Another plug of glass wool was inserted to isolate the adsorbent material. The packed inlet tube was inserted into the inlet of the Perkin Elmer gas chromatograph.

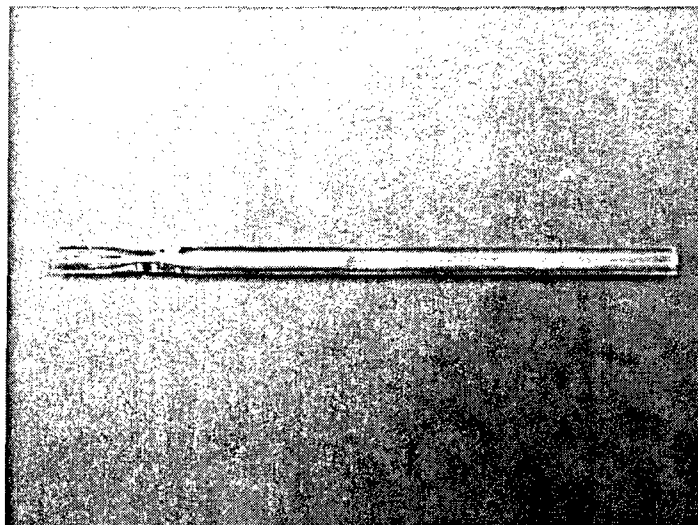


Illustration 1. Perkin Elmer Glass Inlet Tube

A solution (50% wt/wt) of GD (Pinacolyl methylphosphonofluoridate) in carbon tetrachloride was prepared. A 1 μL injection of the solution (the GD concentration was calculated to be 3.58 $\mu\text{mol}/\mu\text{L}$) was injected onto the adsorbent material through injection port and the program started on the gas chromatograph. At the same time, the FTIR program was started. The FTIR program monitors the progression of effluent, which had passed through the column in the gas chromatograph, through the Transfer Line and Light Pipe, into the MCT-A detector. The monitor of the 680 Workstation (in a cascade format) and the Zeta Printer (in multi-step sectional wave-number readout) displayed and recorded the data. After the gas

chromatograph run had ended, the data was processed using a macro called GCX, which generates a Gram-Schmidt reconstructed chromatogram, which can then be analyzed for peaks of interest.

The absorption spectra were recorded between 4000 cm^{-1} and 600 cm^{-1} as percent transmission versus wavenumber using a Nicolet 800 Bench Spectrometer equipped with a mercury-cadmium-telluride (MCT-A) detector ($11,700 - 600\text{ cm}^{-1}$) and a Nicolet 680 Workstation. The spectra were converted to absorbance spectra for analysis and comparison procedures, using the Nicolet 680 Workstation. All measurements were made at 4 cm^{-1} spectral resolution. The digitized data were stored on the 680 Workstation and on diskettes. Spectra were gathered and compared to note the appearance of peaks that would designate the formation of reaction products from the decomposition of agent on the adsorbent.



Illustration 2. Perkin Elmer AutoSystem M Gas Chromatograph with a Nicolet 800 Bench Spectrometer and Nicolet 600 Workstation

3. MATERIALS

Pinacolyl methylphosphonofluoridate (GD), GD-U-2323-CTF-N, purity 98.8%, was provided by the Chemical Agent Transfer Facility, U.S. Army Edgewood Chemical Biological Center. Dr. Mark Mitchell, Clark Atlanta University, provided the alumina-supported cerium oxide (12% based on weight of Ce^{+2} on UOP VGH 22). The alumina (VGH 22, lot number 4426000025) used as a reference material in this study was obtained from UOP, P. O. Box 1031, Baton Rouge, Louisiana, 70821. The alumina was tested as received. Carbon tetrachloride (Lot AK352) was purchased from Burdick & Jackson.

4. INSTRUMENTATION

The micro-reactors consisted of an adsorbent packed on column inlet sleeve (SUPELCO Lot 040403, catalog number 2-6315,05) for Perkin Elmer PSS inlet and an inlet sleeve (2 mm) split for PE PSS inlet (SUPELCO lot 013103, catalog number 2-6315,05). The Perkin Elmer AutoSystem M Gas Chromatograph was connected to the Nicolet 800 Bench Spectrometer with MCT-A detector ($11,700 - 600 \text{ cm}^{-1}$) through a Nicolet 60 SXR GC/Interface. The FTIR spectra were acquired and processed by a Nicolet 680 Workstation. The GC operating parameters were as follows: inlet temperature 25°C , initial oven temperature and ramp $25^\circ\text{C} - 170^\circ\text{C}$ @ $10^\circ\text{C}/\text{min}$, and the oven held at @ $170^\circ\text{C} = 10 \text{ min}$. The column was an RTX-1, ID 0.53, 30-meter (RESTEC). The system included a NICOLET 60 SXR GC/Interface; the Light Pipe temperature was 125°C and the transfer line temperature was 100°C .

The adsorbent in the column inlet sleeve was extracted with 1 mL acetonitrile (Aldrich 99+% HPLC grade, lot 13429PG). Solution was filtered through a 0.45 μm Gelman GHF acrodisc syringe filter and reacted with 50 μL BSTFA (Supleco lot LA845175) at 60°C for 30 minutes. Derivatized samples were analyzed on a Hewlett-Packard 5972 GC/MSD equipped with a 25 m x 0.25 mm Rtx-5 ms column (film 0.25 μm). Injection temperature was 250°C , interface temperature 280°C , and source temperature 150°C . The oven temperature was programmed from $60\text{--}280^\circ\text{C}$ at $15^\circ\text{C}/\text{min}$. The mass range was scanned from 40-500 amu (0.545 s/scan).

5. RESULTS

The results for the decomposition of GD on the alumina supported cerium oxide are shown in Table 1. In reaction 1, GD solution (10 μL) was injected over $\text{CeO}_2/\text{alumina}$ (48.6 mg) before break-through occurred. The total amount of GD injected on the adsorbent was 35.8 μmol . The GC/MS analysis of the adsorbent detected 65.2 area % of GD not decomposed. The major reaction products were methyl-phosphonic acid (13.3 area %) and dipinacolyl methylphosphonate (13.6 area %). The extent of GD decomposition in reaction 2 was much higher. GD break-through occurred after 9 μL of GD solution (32.2 μmol of GD) were injected over 39.9 mg of $\text{CeO}_2/\text{alumina}$. The amount of GD that did not react was 2.8 area %; the major products were dipinacolyl methylphosphonate (52.0 area %), and pinacolyl methylphosphonic acid (27.6 area %). Also in reaction 2, two new products were detected, diisopropyl methylphosphonate (9.4 area %) and isopropyl pinacolyl methylphosphonate (8.1 area %). The calculated amounts of GD decomposed in reactions 1 and 2 were 256 $\mu\text{mol}/\text{g}$ and 785 $\mu\text{mol}/\text{g}$, respectively.^c The average amount of GD decomposed over $\text{CeO}_2/\text{alumina}$ at 30°C for the two reactions was 521 $\mu\text{mol}/\text{g}$.

^c The calculations were not based on a calibration curve. The calculations assumed that area % is equal to weight %, which is not correct but does provide a good approximation of the extent of reaction. The values have been rounded off to the nearest whole number.

Table 1. Decomposition of GD on CeO₂/Alumina

R.T.* (Min)	COMPOUND	REACTION 1	REACTION 2
		Area %	Area %
4.69, 4.73	GD	65.2	2.8
4.95	Diisopropyl methylphosphonate (DIMP)	0	9.4
5.59	Methylphosphonic acid (MPA)	13.3	0.2
6.92, 6.98	Isopropyl pinacolyl methylphosphonate	0	8.1
7.20	Pinacolyl methylphosphonic acid (GD acid)	7.9	27.6
8.90	Dipinacolyl methylphosphonate	13.6	52.0

* R.T. is gas chromatograph retention time.

The results for the reaction of GD on UOP alumina are shown in Table 2. In reaction 3, 16 μ L of GD solution (57.3 μ mol of GD) were injected in the alumina bed before break-through occurred. The GC/MS analysis detected GD (21.8 area %). The major reaction product was the hydrolysate, pinacolyl methylphosphonic acid (74.9 area %). The calculated amount of reacted GD on UOP alumina was 995 μ mol/g. In reaction 4, 12 μ L of GD solution (42.9 μ mol of GD) were injected before break-through occurred in the alumina (52.9 mg) bed. The amount of GD and products on the alumina after break-through was not determined.

Table 2. Decomposition of GD on UOP Alumina

R.T.* (Min)	COMPOUND	REACTION 3	REACTION 4
		Area %	Area %
4.70	GD	21.8	NA
5.57	Methylphosphonic acid (MPA)	1.4	NA
7.19	Pinacolyl methylphosphonic acid (GD acid)	74.9	NA
8.89	Dipinacolyl methylphosphonate	1.8	NA

* R.T. is gas chromatograph retention time. NA is not available.

Pinacolyl methylphosphonic acid was detected on CeO₂/alumina and alumina indicating that the reaction of GD with surface hydroxyls resulted in the substitution of fluorine. However, two of the major products, methylphosphonic acid and dipinacolyl methylphosphonic acid, indicate that the reactions on CeO₂/alumina occurred by an additional mechanism to that on UOP alumina. There is evidence that GD coordinated to Ce⁺² via the phosphonyl oxygen is more susceptible to P-O bond cleavage by surface hydroxyls. Coordination of GD to Ce⁺² could result in a lower electron density around the phosphorous atom compared to P=O coordinating with Al⁺³. The resultant alkoxy group (a product of hydrolysis) then reacts with a second molecule of GD to yield dipinacolyl methylphosphonic acid. However, if this hypothesis is correct the amount of methylphosphonic acid in reaction 2 should be greater. The GD decomposition products DIMP and isopropyl pinacolyl methylphosphonate (Table 1, reaction 2) were due to the presence of isopropanol on the adsorbent. A sample of the CeO₂/alumina was analyzed using a Perkin Elmer TurboMatrix ATD and Agilent Technologies 6890 Network GC System with FID to determine any residual solvents from the preparation of the adsorbent. Isopropanol was tentatively identified by comparing the peak retention time (2.09 min) with a reference chromatograph.

6. CONCLUSIONS

The average amount of GD decomposed on the CeO₂/alumina adsorbent was 521 μmol/g, which was much less than the amount decomposed in one reaction on alumina (995 μmol/g). Based on product analysis, hydrolysis involving fluorine substitution was the major reaction mechanism on alumina and a major mechanism on CeO₂/alumina. At least one additional decomposition mechanism was involved on CeO₂/alumina that was not present on alumina. There was evidence that P-O bond cleavage occurred on CeO₂/alumina and that the pinacolyl group reacted with a second GD molecule to yield dipinacolyl methylphosphonate. There was no evidence of P-C bond cleavage on CeO₂/alumina.

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